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First-principles study of the structure of methanethiolate on Ag(111)

Guo-min He
Department of Physics, Xiamen University, Xiamen 361005, China

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We have systematically investigated the adsorption of methanethiolate (CH_3S) on the Ag(111) surface employing density-functional theory. Various adsorption geometries have been considered and the energetically most favorable structure of CH_3S/Ag(111) was identified. Though the calculated structural parameters for the layer spacing of the adsorbate relative to the nearest Ag layer and the S-Ag bond lengths are reasonable consistent with the experimental results, difference exists about the height corrugation in the S layer. Our results show that the buckling of the S layer observed in experiment might not represent the true atomic positions.

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I. INTRODUCTION

Self-assembled monolayers (SAMs) of organic molecules on metal surfaces[1,2] have attracted much attention for their potential applications in many areas, such as molecular electronic devices, functionalization of metal surfaces, chemical sensors, and biocompatible coatings. For a SAMs system it generally consists of two parts: the molecule-substrate interface where the molecules interact with the substrate through a headgroup, and a chain part that constitutes the outer surface of the molecular layer. Accordingly, two types of interactions are involved: the molecule and substrate interaction in the interface region, and the intermolecular interaction between the chain parts. In general, the detailed structure of the molecule-metal interface is determined by a balance between these interactions. Knowledge of the molecule-metal interface structure is relevant to understanding these interactions which are indispensable for understanding the self-assembled mechanisms and the electronic properties of SAMs. Therefore, a few studies have been performed recently with the aim to establishing the detailed structure of the molecule-metal interface. For example, the structure of $(\sqrt{3}\times\sqrt{3})$-CH_3S/Au(111) phase has been studied by photoelectron diffraction[3] and x-ray standing wave.[4] It was found that CH_3S is located at the top sites. For the case of CH_3S/Cu(111) system, high-resolution photoelectron spectroscopy, x-ray standing wave and scanning tunneling microscopy (STM) studies[5–7] suggested the coexistence of low- and high-temperature thiolate phases in addition to an atomic sulfur phase at room temperature.

Recently, an experimental analysis using STM and low-energy electronic diffraction (LEED) has been performed on the CH_3S/Ag(111) surface.[8] It was found that an ordered methanethiolate structure was formed on the Ag(111) surface by reaction with dimethyl-disulfide (CH_3S-SCH_3) at the room temperature. Some special features have also been demonstrated for the CH_3S/Ag(111) surface: (i) Distinctly different from the $(\sqrt{3}\times\sqrt{3})$-CH_3S/Au(111) phase, a well-ordered $(\sqrt{7}\times\sqrt{7})R19°$-$CH_3S$/Ag(111) structure was observed. For such phase it consists of three distinctly different S sites relative to the underlying Ag substrate which were shown as corresponding to the top, hexagonal close packed (hcp), and fcc hollow sites. This is rather surprising because for most simple adsorbates on the fcc(111) surfaces there are large energy differences between the top and two inequivalent hollow sites. (ii) The STM images provided evidence that CH_3S causes the surface Ag layer to reconstruct. For atomic adsorbates, it is a well-known phenomenon that adsorption induced surface rearrangement can occur. It is relatively unexplored involving a molecular adsorbate. (iii) The STM images also showed that there is a height variation for CH_3S at different adsorption sites which is about 0.3 Å, though there is no simple direct correlation between the height variations in the STM images and in the true atomic positions. In order to obtain the quantitative information on the interface structure of the $(\sqrt{7}\times\sqrt{7})R19°$-$CH_3S$/Ag(111) surface phase, further investigation has been performed by normal-incidence x-ray standing wave (NIXSW) analysis.[9] The main results are as follows. (i) The resulting NIXSW structural parameter values clearly excluded any adsorption model on the clean Ag(111) surface (i.e., without reconstruction). (ii) A reconstructed surface model was proposed that comprises a near-hexagonal Ag surface layer with an Ag density of only 3/7 that of the underlying substrate layers, and all the CH_3S molecules are adsorbed into the hollow sites of the reconstructed Ag layer which correspond to the top, fcc, and hcp sites relative to the underlying unreconstructed substrate. Though the proposed model is consistent with the NIXSW measurements and with the STM observation, the question still remains because the reconstructed Ag layer is planar, all the CH_3S molecules are expected to have the same layer spacing to the Ag substrate. This is inconsistent with the experimental results because the corrugation of the S layer was suggested to be about 0.3 $\sim$0.5 Å by the NIXSW measurement.

In contrast, theoretical studies of CH_3S on the Ag surface are rather limited. Virtually little is known about how CH_3S is incorporated at the surface and formed the SAMs' structure. To our knowledge, only a few theoretical studies of CH_3S/Ag(111) SAMs exist.[10–12] In these studies CH_3S adsorption on the Ag(111) surface was modeled by a two-layer thick closest-packed cluster or by a slab with four metal layers. However, the interface structure of CH_3S/Ag(111) has not been studied. Though some features of the interface structure have been revealed by experiment,[8,9] the detailed interface structure of CH_3S/Ag(111) still remains controver-

sial. In order to better understanding these issues we have studied the adsorption of CH_3S on the Ag(111) surface employing density-functional theory. In the present work we focus mainly on the interaction of CH_3S with the Ag(111) surface for various CH_3S adsorption geometries as a first step towards the understanding of the CH_3S/Ag(111) interface structure. The adsorption of CH_3S on the Ag surface is also of fundamental interest in relation to understanding these SAMs more generally.

This paper is organized as follows. The calculation method is given in Sec. II. Section III presents the calculated results. Finally, a brief summary is given in Sec. IV.

II. METHOD OF CALCULATION

The density-functional theory total-energy calculations were performed with the SIESTA code (Ref. 13) within the local-density approximation (LDA). The Ceperley-Alder form of exchange and correlation energy function was used. The ion and core electrons were replaced by norm conserving pseudopotentials in their fully separable form, and numerical atomic orbitals were used as the basis sets.[14] We chose double ζ atomic orbitals plus polarization orbitals as the basis sets with an equivalent plane-wave cutoff of 180 Ry to represent the charge density.

The surface is modeled by a four-layer slab separated by an 18-Å vacuum space and CH_3S is placed on one side of the slab. The positions of the top two Ag layers and the CH_3S molecules were allowed to relax until the forces were less than 0.03 eV/Å, while the bottom two layers of Ag were held fixed in their bulk positions. In the (1×1) surface unit cell, more than 38 special k points were used in the surface irreducible Brillouin zone for the Brillouin-zone integration.

The stability of various CH_3S/Ag(111) structures is analyzed with respect to the adsorption energy. The adsorption energy is defined as[15]

$$E_{ads} = \frac{1}{n}[E^{slab}_{n\mathrm{CH_3S/Ag}} - E_{n\mathrm{CH_3S}} - E^{slab}_{\mathrm{Ag}}], \quad (1)$$

where n is the number of the adsorbed molecules, and $E^{slab}_{n\mathrm{CH_3S/Ag}}$ is the total energy of the CH_3S/Ag(111) surface under consideration, while $E_{n\mathrm{CH_3S}}$ is the total energy of n CH_3S gas-phase molecules which used the same geometries of the adsorbed molecules—i.e., without optimization, and spin-polarization was used. E^{slab}_{Ag} is the total energy of the reference system—i.e., the clean surface for the unreconstructed model and reconstructed surface for the reconstructed model. Note that (i) the energy required to form the reconstructed Ag(111) surface is not included and (ii) the error due to the basis set superposition error (BSSE) has been corrected by the counterpoise corrections—i.e., the same basis set as the total system $n$$CH_3S$/Ag(111) has been used to calculate the total energies of the separate substrate E^{slab}_{Ag} and adsorbate $E_{n\mathrm{CH_3S}}$.[16–18] According to the definition, E_{ads} can be regarded as the energy required to separate the adsorbed system CH_3S/Ag(111) into two noninteracting parts: the Ag(111) surface and n CH_3S molecules.

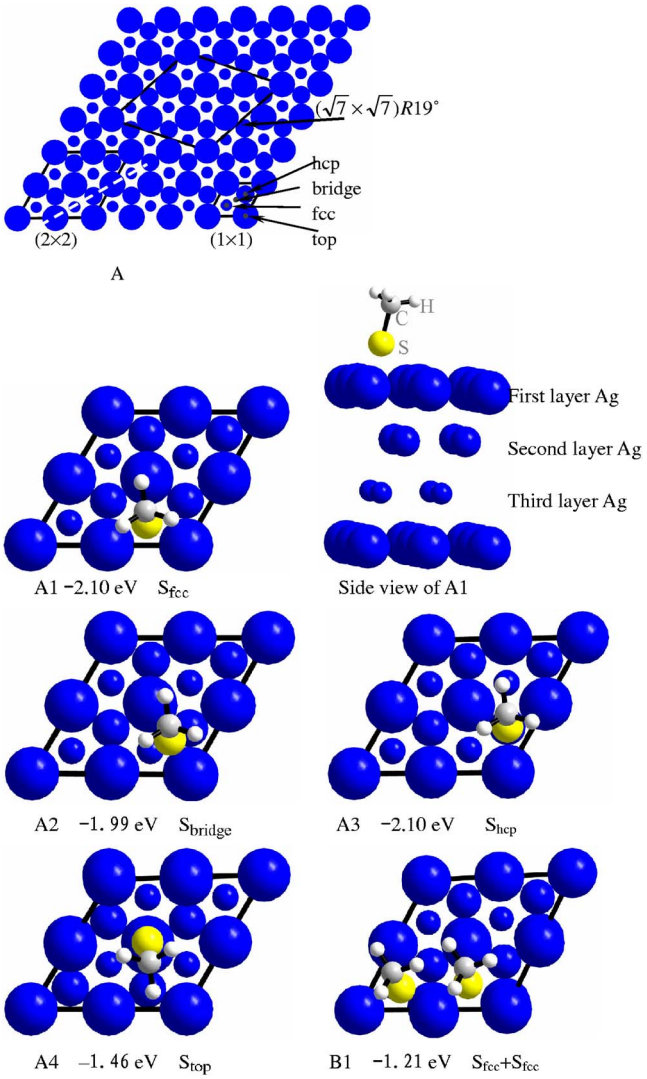

FIG. 1. (Color online) (A) Top view of the Ag(111) surface. The large, middle, and small circles denote the first layer, second layer, and third layer Ag atoms. The (1×1), (2×2), and $(\sqrt{7}\times\sqrt{7})$R19° surface unit cells were also indicated. The adsorption sites were represented by the small black dots. The dashed line indicates the studied path. (A1)–(B1) Examples of adsorption with one and two methanethiolate molecules within the (2×2) unit cell. The adsorption energies and location of the headgoup S atom are also indicated. For example, S_{fcc} corresponds to thiolate with the S headgroup at the fcc site of the substrate lattice.

For CH_3S adsorption on the clean Ag(111) surface, we also calculated the molecule-molecule interaction $E_{mol\text{-}mol}$ as follows:

$$E_{mol\text{-}mol} = \frac{1}{n}[E^{slab}_{n\mathrm{CH_3S/Ag}} - nE_{1\mathrm{CH_3S/Ag}} + (n-1)E^{slab}_{\mathrm{Ag}}],$$

where $E_{1\mathrm{CH_3S/Ag}}$ is the total energy of surface with a single CH_3S adsorbed molecule [e.g., the structure of Fig. 1(A1)]. According to the definition, $E_{mol\text{-}mol}$ can be regarded as the energy required to dissociate $E^{slab}_{n\mathrm{CH_3S/Ag}}$ into n noninteracting $E_{1\mathrm{CH_3S/Ag}}$ parts. It is also defined such that a positive value

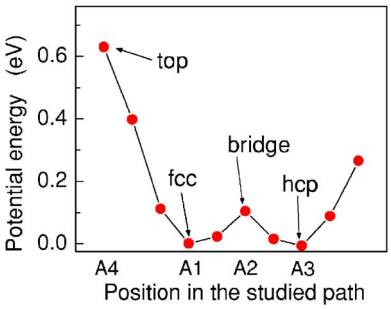

FIG. 2. (Color online) The total energy difference for a single CH_3S molecule on Ag(111) at different positions along the studied path. The studied path was indicated by the dashed line in Fig. 1(A).

indicates that the interaction is repulsive and a negative value indicates that the interaction is attractive.

The bulk equilibrium properties for Ag have been verified in a previous study.[19] Additional calculations of the relevant gas phase molecules CH_3SH and CH_3S-SCH_3 were performed giving the geometries in reasonable agreement with experiment. In addition, test calculations have been performed to check the convergence with respect to the k point set, slab size, and vacuum thickness. We found that the adsorption energies converged to an accuracy of about 0.1 eV/molecule with respect to an eight-layer slab. We also performed test calculations using generalized gradient approximations (GGA) and found that the relative stability between structures was almost unaffected. However, the structural parameters obtained by the GGA were about 2–3 % larger than those by the LDA. We chose the LDA in this work because its structural parameters agree more with the available experimental values than the GGA's.

III. RESULTS AND DISCUSSIONS

A. CH_3S adsorption on the unreconstructed Ag(111) surface

As a starting point, we studied the adsorption of CH_3S on the unreconstructed Ag(111) surface using a (2×2) surface unit cell. Knowledge of the adsorption site and adsorption structure is the first step towards a detailed understanding of the SAMs' structure on Ag(111). Therefore we calculated the energy profiles for a single CH_3S molecule in the (2×2) surface unit cell. In the calculation, the CH_3S molecule was placed in a succession of locations. The head S atom of the CH_3S molecule interacting with the Ag(111) surface was allowed to relax only in the direction normal to the surface. The studied path was indicated by the dashed line in Fig. 1(A)—i.e., the thiolate was moved from top [Fig. 1(A4)] to fcc [Fig. 1(A1)], then over the bridge [Fig. 1(A2)] to the hcp site [Fig. 1(A3)]. The results were shown in Fig. 2. They were calculated as the total-energy difference between a CH_3S molecule at a given site and at the most stable adsorption site (i.e., the fcc site). Our results show that (i) the threefold fcc and hcp hollow sites are the most stable adsorption sites with almost the same adsorption energies and (ii) the top sites, bridge sites, or the low symmetry sites, that are intermediate between the bridge and threefold hollow sites are all less stable than the threefold hollow sites. The optimized atomic geometries and the adsorption energy were also listed in Table I. The bridge site is only 0.11 eV less stable than the threefold hollow sites, indicating that the adsorption potential energy surface (PES) is relatively flat. The top site is the most unfavorable adsorption site which is disfavored by about 0.64 eV than the fcc site. It is of interest to compare the results presented above with those of CH_3S/Cu(111) and CH_3S/Au(111). The PES for CH_3S/Cu(111) was extremely shallow: the bridge site was only 0.01 eV less favorable than the fcc site, whereas the top site was 0.5 eV above the fcc site.[20] The PES for CH_3S/Au(111) displayed some distinctly different features: the fcc site was 0.4 eV more favorable than the bridge site, and 0.95 eV more favorable than the top site.[21] It has been argued that the more ionic bonding of thiolates with Cu would have a much less directional character than with gold,[20] qualitatively explaining the flat PES of CH_3S/Cu(111). Accordingly, the flat PES for CH_3S/Ag(111), which was very similar to CH_3S/Cu(111), suggests that the thiolates-Ag bonding would have more ionic character than covalent character. This ionic bonding picture for CH_3S/Ag(111) will be confirmed from the electron density plots below. It is worth mentioning that the long-range van der Waals (vdW) interactions, which may play an important role in the SAMs formation, were not included in our calculation. However, the vdW interaction may be less strong for methanethiol than for thiolates with longer tail chains because methanethiol is the simplest alkanethiol.

TABLE I. The calculated adsorption energies and surface geometries of 0.25 ML CH_3S adsorption at different surface sites on Ag(111). Here, ΔE_{ads} denotes the relative adsorption energy difference with respect to the structure shown in Fig. 1(A1). d_z is the vertical distance between the S atom and the first surface Ag layer, r(S-Ag) is the S-Ag bond distance and θ is the tilt angle of the S-C bond away from the surface normal direction.

Adsorption site	E_{ads} (eV)	ΔE_{ads} (eV)	d_z (Å)	r(S-Ag) (Å)	θ (°)
fcc [Fig. 1(A1)]	−2.10	0.0	1.98	2.59	12.7
hcp [Fig. 1(A2)]	−2.10	0.0	1.98	2.59	12.7
Bridge [Fig. 1(A3)]	−1.99	0.11	2.02	2.52	14.8
Top [Fig. 1(A4)]	−1.46	0.64	2.33	2.43	19.0

To date, theoretical studies of thiolate-Ag(111) are rather limited. The adsorption energy reported by Akinaga *et al.*[10] using a two-layer thick cluster was calculated to be 46.94 kcal/mol (2.03 eV). The S-Ag bond length was determined to be 2.60 Å. More recently, Cometto *et al.*[11] obtained a value of 39.58 kcal/mol (1.72 eV) with the same cluster model and a value of 47.1 kcal/mol (2.04 eV) using a $(\sqrt{3}\times\sqrt{3})$-Ag(111) slab model. The S-Ag bond length was found to be about 2.555 Å. The calculation by Sellers *et al.*[12] reported the shortest S-Ag bond length (2.33 Å) using a cluster model at Hartree-Fock-electron correlation level. Our value for the adsorption energy (S-Ag bond length) was calculated to be 2.10 eV (2.59 Å) for the fcc site, reasonably consistent with the results of Akinaga and Cometto. The deviation of

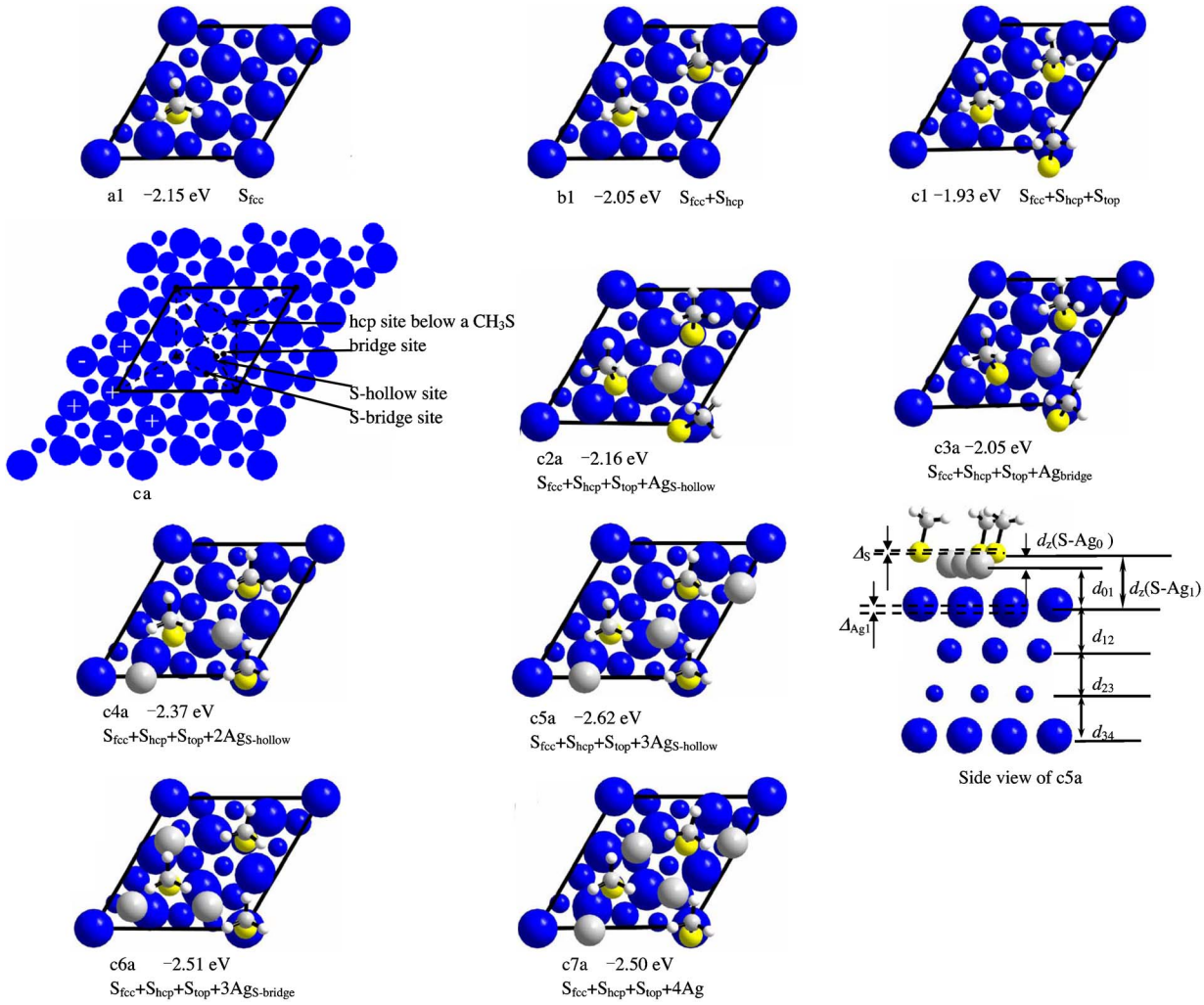

FIG. 3. (Color online) Examples of adsorption within the $(\sqrt{7}\times\sqrt{7})$R19° surface unit cell: a1–c1 on the unreconstructed Ag(111) surface, and c2a–c7a on the reconstructed Ag(111) surface. The adsorption energies and location of the head S and Ag adatoms are also indicated. Note that some S atoms have lateral displacement from the location indicated. For reconstructed model the large gray balls denote the Ag adatoms. In ca, the S-hollow and S-bridge sites for the Ag adatoms were indicated, which assumed that three CH_3S molecules occupy the ideal top, fcc, and hcp sites, respectively, respective to the Ag substrate. The dashed lines are used to guide the eyes. The minus (plus) sign for surface Ag atoms represents the inwards (outwards) relaxation for the structure of c5a. The CH_3S and Ag adatoms produced by the periodic boundary conditions were omitted for clarity.

Sellers' results may be due to the different type of calculation used. Moreover, it was also found that the adsorption energy difference between the fcc and bridge site is small, of the order of about 0.10 eV.[11]

Next, we added one additional CH_3S molecule to the Ag(111) surface which corresponds to the CH_3S coverage of 0.5 ML (1.0 MLs means one CH_3S molecule per one surface Ag atom). Four adsorption sites were considered for locating the two CH_3S molecules: the fcc, hcp, bridge, and top sites. The nearest distance between two head S atoms now becomes about 2.9 Å [Fig. 1(B1)]. The fcc sites were the most stable sites with a adsorption energy of −1.21 eV [Fig. 1(B1)]. Compared to −2.10 eV for the structure of Fig. 1(A1), it can be seen that the adsorption energies for the structure of Fig. 1(B1) decrease by 0.89 eV, indicating a repulsive interaction between the CH_3S molecules. To gain deeper insight into the bonding mechanism for CH_3S adsorption on the Ag(111) surface, we also calculated the molecule-molecule interaction $E_{mol\text{-}mol}$ for the structure of Fig. 1(B1) with respect to the structure of Fig. 1(A1), and obtained a value of 0.78 eV, suggesting that the repulsive interaction between two CH_3S molecules is the key factor of energy loss. It is worth mentioning that the difference in adsorption energy between the top and fcc site becomes less as the coverage increases. Compared to 0.64 eV/molecule at the CH_3S coverage of 0.25 ML (cf. Table I), it reduces to 0.20 eV/molecule.

B. Interface structure of CH_3S/Ag(111)

As guided by the experimental results, we now use a larger surface unit cell in the calculation—i.e., a $(\sqrt{7}\times\sqrt{7})$R19° surface unit cell. We first considered the adsorption on the unreconstructed Ag(111) surface with one, two,

and three CH_3S molecules. Structure optimizations were performed for a variety of initial geometries in order to identify the most favorable structure at given CH_3S coverages. These included geometries with different adsorption sites, different orientation of molecule, and different distance between two molecules. The respective most favorable structures are shown in Figs. 3(a1)–3(c1). The adsorption energy for one CH_3S molecule occupying the fcc site [Fig. 3(a1)] was calculated to be −2.15 eV, which is 0.05 eV more favorable than that at CH_3S coverages of 0.25 ML [Fig. 1(A1)]. We also see that the overall variation in the magnitude of the adsorption energies is only 0.22 eV when the CH_3S coverage varies from 1/7 to 3/7 ML. Compared to the variation of 0.89 eV for the CH_3S coverage changing from 0.25 to 0.50 ML, it suggests that the repulsive molecule-molecule interaction for these structures becomes less. Note that the CH_3S molecule adsorbed at the top site [Fig. 3(c1)] was laterally displaced from the precise top site by about 0.92 Å. This is not hard to understand because the top site is the most unfavorable adsorption site on the clean Ag(111) surface (cf. Table I). Test calculations also shows that the adsorption energy decreases markedly for structures with the S-S distance of less than 4.0 Å. Dimerization of CH_3S on the surface—i.e., forming dimethyl-disulfide (CH_3S-SCH_3), is energetically unfavorable [more than 1.75 eV unfavorable than the structure of Fig. 3(b1)].

From the results above, we found that the structure shown in Fig. 3(c1) does not correspond to the $(\sqrt{7}\times\sqrt{7})R19°$ phase found in the experiment because both the LEED and STM analyses revealed that within the $(\sqrt{7}\times\sqrt{7})R19°$ unit cell one of the CH_3S molecules occupied the top site.[8] In order to stabilize the CH_3S molecule adsorption at the top site, we reconstructed the Ag(111) surface by adding Ag adatoms to the surface. A number of structures containing up to four Ag adatoms were considered. We began by adding one Ag adatom to the surface. All possible adsorption sites for the Ag adatom were tested including the available fcc, hcp, bridge, and fcc (or hcp) site below a CH_3S molecule, bridge sites between two head S atoms (denoted as S bridge), and hollow site of the S layer (denoted as S hollow) [cf. Fig. 1(A) and Fig. 3(ca)]. Initially both the CH_3S molecules and the Ag adatom were placed 3.0 Å above the Ag substrate which is about 0.6 Å above the ideal layer spacing of Ag substrate. For Ag adatom adsorption at the fcc (or hcp) site below a CH_3S molecule, the CH_3S molecules were placed 5.5 Å above the Ag substrate. Then the whole system except the bottom two Ag layers was allowed to relax without constraint. The main results are as follows. (i) The S-hollow site is the most stable adsorption site for the Ag adatom. (ii) The Ag adatom adsorption on other sites, such as fcc, hcp, and bridge sites, tends to relax towards the S-hollow site. If the Ag adatom was constrained to relax only in direction normal to the surface plane, the bridge site [Fig. 3(c3a)] is 0.33 eV less stable in total energy than the S-hollow site. (iii) The fcc (or hcp) site below a CH_3S molecule is the most unfavorable adsorption site for the Ag adatom. After optimization it leaded to a tilt structure that was disfavored by about 1.50 eV in total energy than the S-hollow site. Therefore the adsorption sites below a CH_3S molecule were excluded for further consideration.

TABLE II. The main geometrical parameters in Å for the structure of Fig. 3(c5a). Here, Ag0 and Ag1 represent the Ag adatom layer and the first substrate Ag layer, respectively. Δ_S and Δ_{Ag1} denote the magnitude of the buckling of the S layer and of the first Ag layer, respectively. d_z and d_{ij} represent the interlayer distances while r(S-Ag) denotes the S-Ag bond distances. For the interlayer distances, the center of mass of the layer is used. Numbers in parentheses correspond to bulk values, which were fixed.

	Fig. 3(c5a)	Expt.[a]
Δ_S	0.10	0.3–0.5
Δ_{Ag1}	0.30	
d_z(S-Ag0)	0.640	0.52±0.03
d_z(S-Ag1)	3.040	
d_{01}	2.400	
d_{12}	2.455	
d_{23}	2.425	
d_{34}	(2.367)	
r(S-C)	1.839	
$r(S_{top}$-Ag0)	2.676	2.70
$r(S_{hcp}$-Ag0)	2.665	
$r(S_{fcc}$-Ag0)	2.621	
$r(S_{top}$-Ag1)	2.946	
$r(S_{hcp}$-Ag1)	3.388	
$r(S_{fcc}$-Ag1)	3.560	

[a]References 8 and 9.

We next added a second Ag adatom to the surface. All site combinations of the possible adsorption sites for the two Ag adatoms were taken into account (the same procedure was followed to simulate the adsorption of three and four Ag adatoms). The most stable structure is shown in Fig. 3(c4a). Comparing −2.16 eV for the structure of Fig. 3(c2a) to −2.37 eV for the structure of Fig. 3(c4a), the adsorption energies increase by about 0.21 eV, suggesting that the Ag adatoms can stabilize the CH_3S molecules.

For the case of three Ag adatoms, the structure of Fig. 3(c5a) turns out to be the most stable structure with an adsorption energy of −2.62 eV, about 0.69 eV more favorable than in the case of unreconstruction [−1.93 eV for the structure of Fig. 3(c1)]. Note that the energy required to form the reconstructed Ag(111) surface was not included. We also studied an ideal process of creating an Ag vacancy on the clean Ag surface. Such vacancy formation energy was calculated to be about 0.65 eV with respect to bulk Ag. Therefore even adding this energy cost to the adsorption energy, the structure of Fig. 3(c5a) still favors by 0.04 eV over the structure of Fig. 3(c1). The main feature for the structure of Fig. 3(c5a) is that all the Ag adatoms form a hexagonal commensurate structure within the $(\sqrt{7}\times\sqrt{7})R19°$-Ag(111) surface unit cell. It should be emphasized here that the CH_3S molecule which is laterally relaxed from the top site for the structure of Fig. 3(c1) now occupies almost the precise top site (lateral relaxation less than 0.01 Å). If all three Ag adatoms adsorption at the S-bridge sites were not allowed to relax laterally [Fig. 3(c6a)], it was 0.11 eV (0.33 eV in total energy) less stable than the structure of Fig. 3(c5a).

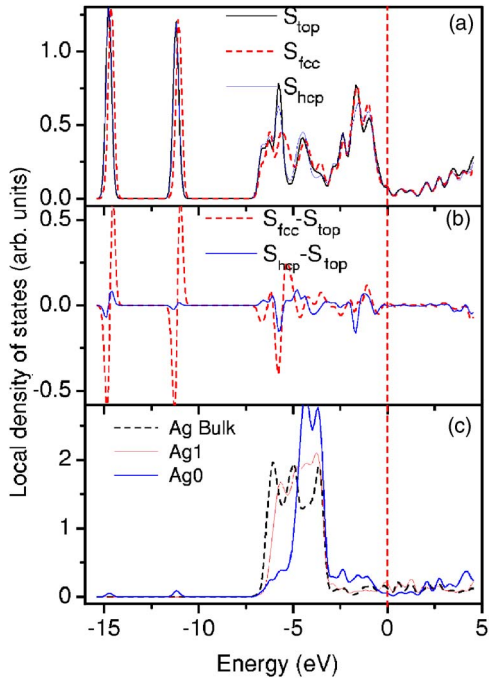

FIG. 4. (Color online) The local density of states (LDOS) for the S and Ag atoms for the structure of Fig. 3(c5a). The difference of LDOS for S_{fcc} and S_{hcp} relative to S_{top} was plotted in (b). In (c), Ag0 and Ag1 represent the Ag adatom layer and the first substrate Ag layer, respectively. The Fermi level is set to the energy zero.

Finally, we considered the adsorption of four Ag adatoms. If all four Ag adatoms occupy the S-hollow sites within the surface unit cell, the nearest distance between two Ag adatoms is about 2.6 Å while it is about 2.9 Å for the ideal substrate, indicating that the local Ag density for the Ag adatom layer is slightly larger than the substrate layer. After optimization the common feature of the resulting structures is that the Ag adatoms relaxed away from the precise S-hollow sites slightly while the CH_3S molecules also displaced slightly from the respective fcc, hcp, and top site [Fig. 3(c7a)]. Compared to four Ag adatoms occupying the precise S-hollow sites, the relaxed structure [Fig. 3(c7a)] was 0.20 eV (0.61 eV in total energy) more stable. As suggested by the NIXSW measurement, we only considered simple overlay of Ag adatoms on the clean Ag(111) surface. Therefore the possibility of reconstruction with multilayer structure can not be ruled out.

Of all the structures studied, we found that the structure shown in Fig. 3(c5a) turns out to be the most stable structure, which was also suggested to be the most possible interface structure by the NIXSW measurements.[9] It is worth mentioning that the stability of the most relevant structures was tested by two extra sorts of calculations. In one calculation, both the CH_3S molecules and Ag adatoms were separated 1.5 Å more apart (in z direction) from the resulting geometries. The other calculation was similar to the first one except that the CH_3S molecules or Ag adatoms were laterally displaced (in the xy direction) by about 0.15 Å. Then structural optimizations were performed again. After optimization it leads to almost the same structure as well as a few metastable structures. Therefore a proposed structural model[9] with the Ag adatoms lateral displacement by 0.15 Å is not appropriate. We also studied the adsorption of a single Ag adatom on the bare Ag(111) surface. The most stable adsorption sites are the fcc and hcp hollow sites. The bridge site is only 0.06 eV less favorable, indicating the PES for the Ag adatom is even more flatter than that for a CH_3S molecule (0.11 eV, cf. Table I). This implies that the positions of Ag adatom relative to the substrate are not of crucial importance and can be stabilized by the S-Ag bonding within the reconstructed layer. Namely, the interface structure of $CH_3S/Ag(111)$ is determined to a large extent by the strength of S-Ag interaction.

The main geometrical parameters of the structure shown in Fig. 3(c5a) were given in Table II. The determined layer spacing of the adsorbate relative to the Ag adatom layer $d_z(S\text{-}Ag_0)$ (0.640 Å) and the S-Ag bond lengths $r(S\text{-}Ag_0)$ (2.65 Å) agree reasonably well with the experimental data (0.52±0.03 Å and 2.70 Å, respectively). However, we do note that the height corrugation of the S layer Δ_S (0.1 Å) is clearly inconsistent with experimental data (0.3–0.5 Å). Instead, we found that the corrugation of the first Ag layer Δ_{Ag1} was quite large, about 0.3 Å. The relaxed patterns were indicated in Fig. 3(ca). Among the seven substrate Ag atoms within the surface unit cell, three Ag atoms below the S_{fcc} atom were relaxed inwards by about 0.025 Å while the other four atoms (i.e., three Ag atoms below the S_{hcp} atom and one Ag atom below the S_{top} atom) were relaxed outwards by about 0.278 Å (averaged by four Ag atoms). We note that the large corrugation of first Ag layer Δ_{Ag1} was also found by a recent study[11] (about 0.31 Å using a cluster model with 25 Ag atoms). It is worth noting that in the theoretical fits for

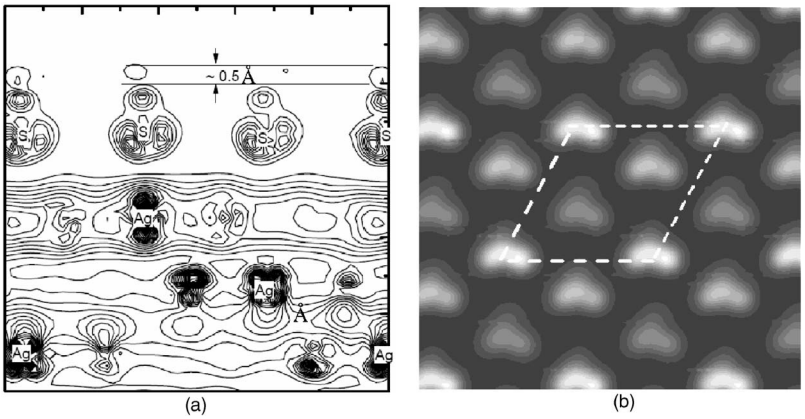

FIG. 5. Contour plots of local density of states (LDOS) at the Fermi level for the structure shown in Fig. 3(c5a). The LDOS was integrated around the Fermi level from −0.2 to 0.05 eV. (a) and (b) represent the cross sections in planes perpendicular and parallel to the Ag(111) surface, respectively. The perpendicular plane was taken to include the S atoms while the parallel plane was cut at 1.0 Å above the outermost C atoms. The distance between contours is 1×10^{-4} $e/Å^3$ (left) and 1.5×10^{-5} $e/Å^3$ (right). The corrugation of LDOS and the $(\sqrt{7}\times\sqrt{7})R19°$ surface unit cell were indicated in (a) and (b), respectively.

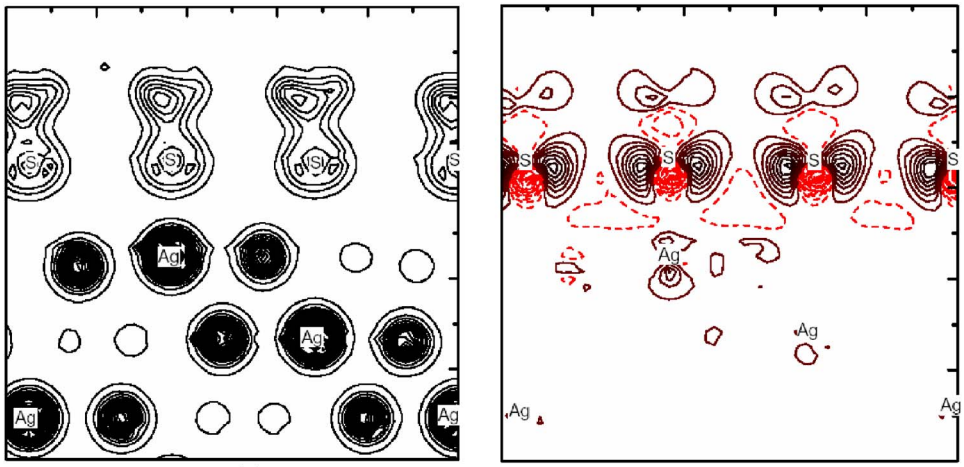

FIG. 6. (Color online) Contour plots of constant electron density in a plane perpendicular to the Ag(111) surface for the structure shown in Fig. 3(c5a): (a) total electron density, (b) electron density difference. The electron density difference is defined by $\Delta\rho(n\mathrm{CH_3S}/substrate) - \rho(n\mathrm{CH_3S}) - \rho(substrate)$. The spacing between contours is 0.4 $e/\text{Å}^3$ (left) and 8×10^{-4} $e/\text{Å}^3$ (right). Positive and negative differences are represented by solid and dashed contours, respectively.

the NIXSW measurements[9] a hard sphere model was adopted which used the ideal interlayer spacing of the Ag substrate—i.e., without taking into account any relaxation of the substrate. This may introduce some errors in the experimental results.

In addition, we note that the bonding environment around the S atoms is different for S_{fcc}, S_{hcp}, and S_{top}. It may affect the strength of interaction between the head S atoms and the Ag atoms. The S-Ag bond strength can affect in turn the spatial distribution of electron density around the Fermi level. To confirm this view, we analyzed the local density of states (LDOS) for the S and Ag atoms for the structure of Fig. 3(c5a). The electronic states centered around 15.0 and 11.5 eV below the Fermi level are dominated by the S 3*s* states [Fig. 4(a)]. The Ag 4*d* states hybridized with S 3*p* states, give contribution mainly in the range of −3.0 to −7.0 eV [Fig. 4(c)]. The LDOS around the Fermi level are dominated mainly by the S 3*p* band. The difference of LDOS for S_{fcc} and S_{hcp} relative to S_{top} was plotted in Fig. 4(b). From this figure one can clearly see that the bonding properties are different for the three S species, though it is hardly discernable around the Fermi level.

The simulated STM image for the $(\sqrt{7}\times\sqrt{7})$R19° SAM structure was presented in Fig. 5, which was calculated by integrating the local density of states around the Fermi level from −0.20 to 0.05 eV. The left and right panels represent the cross sections in planes perpendicular and parallel to the Ag(111) surface, respectively. The perpendicular plane was taken to include the S atoms, while the parallel plane was cut at 1.0 Å above the outermost C atoms. Focusing on Fig. 5(a) one can clearly see the height corrugation. Using an arbitrary spacing of 1×10^{-4} $e/\text{Å}^3$ contour the amplitude of the corrugation was estimated to be of the order of about 0.5 Å, in reasonable agreement with the experiment (cf. Table II). Moreover, the simulated STM image [Fig. 5(b)] is qualitatively consistent with the experimental STM images,[8] in which one molecule in the $(\sqrt{7}\times\sqrt{7})$R19° unit cell is imaged brighter than the other two. It confirms that the spatial distribution of electron density around the Fermi level is really different for the three CH_3S molecules though the height variation is only 0.1 Å. We also noticed that the simulated image for S_{hcp} is slightly different from that for S_{fcc}. Such feature can be really seen in the experimental STM images by using different tunneling voltages and currents. On the basis of the above results we concluded that the structure of Fig. 3(c5a) would be the most possible interface structure of $CH_3S/Ag(111)$ and the height corrugation of the S layer suggested by experiment[8,9] is due to the electronic effects—i.e., different spatial distribution of electronic density was induced by the different S-Ag bond strength.

To further investigate the bonding mechanism for the adsorption of CH_3S molecules on the Ag(111) surface, the total and electron density difference for the structure shown in Fig. 3(c5a) were presented in Fig. 6. The electron density difference was obtained by subtracting the superposition of the electron density of the adsorption molecules CH_3S and the Ag(111) surface from that of $CH_3S/Ag(111)$. Figure 6(b) reveals that the electron density is depleted at the S-Ag bond close to the S atom (S p_z orbitals), while there is a slight increase in the Ag d_z^2 orbitals very close to the Ag atom. Moreover, the electron density in the S $3p_x$ (p_y)-like orbitals increases strongly, and the surface Ag 5*s* electrons, which are in a delocalized shape, are depleted. Therefore the S-Ag bonding is essentially ionic. This is consistent with the previous calculation.[10] It is of interest to compare the results for $CH_3S/Ag(111)$ presented above with those of $CH_3S/Cu(111)$ and $CH_3S/Au(111)$. For the S-Au bond, it was found that the electron density increases mainly in regions halfway between the Au and S atoms, and is depleted near the Au and S atoms, revealing a covalent character.[22] The S-Cu bond was found to be strongly polarized with a charge accumulation near the S atom and a depletion near the Cu atom.[23] This is very similar to the S-Ag bonding picture described above. So the Cu-S bonding is also ionic. In fact, these noble metal-S bonding picture can be explained in terms of a simple electronegativity argument. Given the fact that Au and S are more electronegative than Cu and Ag (the Pauling electronegativitiy for them: Cu 1.90, Ag 1.93, Au 2.54, and S 2.58), it would result in an ionic picture in the S-Cu and S-Ag bonding, and a more covalent and directional picture in the Au-S bonding.

IV. SUMMARY

The adsorption of methanethiolate (CH_3S) on the Ag(111) surface has been investigated by *ab initio* total energy calcu-

lations. Our results show that the interface structure of $CH_3S/Ag(111)$ is determined largely by the molecule-substrate interaction—i.e., the S-Ag bonds. From our results the energetically most favorable structure was identified. The calculated structural parameters for the layer spacing of the adsorbate relative to the nearest Ag layer and the S-Ag bond lengths are in reasonable agreement with the available experimental results. However, the result of 0.10 Å for the height corrugation in the S layer is clearly inconsistent with the experimental value of 0.3–0.5 Å. We explained this discrepancy in terms of the structural and electronic effects.

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[15] Comparing to the following definition $E_{ads}=n^{-1}[E^{slab}_{n\mathrm{CH_3S/Ag}} - nE_{\mathrm{CH_3S}} - E^{slab}_{\mathrm{Ag}}]$, the total energy of n CH_3S was used in Eq. (1). Therefore the molecule-molecule interaction energy is not included.
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